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ABSORPTION OF 7.7 mm MICROWAVES BY SOLUTIONS OF SOME SUBSTITUTED NITROBENZENES IN DIFFERENT NON-POLAR SOLVENTS

(Miss) B. SINHA, S. B. ROY AND G. S. KASTHA

OPTICS DEPARTMENT,

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

CALCUTTA-32.

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ABSTRACT. The absorption of 7.7 mm microwaves by some substituted nitrobenzenes in solutions in CCl_4, C_6H_6, *n*-hexane and paraffin at different temperatures has been investigated and the τ-values for the various polar compounds have been determined. It has been found that while the values of $\frac{\tau T}{\eta}$ in all the cases do not remain constant and increase with increase of temperature, the values of $\frac{\tau . T}{\eta^{\gamma}}$ (where γ is the ratio of the molar heats of activation for dielectric relaxation and viscous flow) for each of the compounds in solutions in different solvents are found to be constants. From these results, it has been concluded that η^{γ} may be taken to be a measure of internal friction.

INTRODUCTION

In deriving the relation $\tau = \frac{4\pi\eta_{int} \cdot a^3}{kT}$ between the time of relaxation (τ) at a certain temperature (T), the internal viscosity (η_{int}) and the radius of the rotating dipole (a), Debye assumed that the moment of the frictional force acting on the rotating dipole is proportional to its angular velocity and the constant of proportionality ζ is given by $\zeta = 8\ \pi\eta_{int}a^3$. The values of '$a$' calculated from the experimentally observed τ-values in many cases differ widely from the dimension of the rotor obtained from the chemical bond data. This difference is attributed to (1) non-sphericity of most of the polar molecules, (2) the inadequacy of the macroscopic viscosity (η) as a measure of the internal friction and (3) non-applicability of the hydrodynamic model of uniform fluid to the solutions possessing macroscopic structure. Fischer (1939, 1949) used the Perrin's (1934) modification of the Debye relation in the case of ellipsoidal molecules and a coefficient of internal friction $\eta_{int} = \text{const.}\ \eta$ to calculate the τ-values for some polar molecules from the dimensions of the molecules and found some agreement with the experimental values of the time of relaxation for these compound in solution in a certain non-polar solvent at a fixed temperature. The agreement is, however, lost when the solvent is changed (Whiffen, 1950; Hase, 1953). Wirtz and his co-workers

(1953a, b) obtained an expression for ζ in case of solutions of spherical polar molecules in solvents composed of spherical molecules in terms of the macroscopic viscosity of the solutions and the ratio of the radii of the two types of molecules. Hill (1954) derived an expression for ζ which depended in a complicated way on the macroscopic viscosities of the solvents, the solute and the solution and also on the various parameters of the solvent and solute molecules. Hase (1953) proposed an empirical relation $\eta_{int} = \eta \exp\left(-\frac{A.V_2}{V_1}\right)$, where V_1 and V_2 respectively are the volumes of the molecules of the solvent and the solute and A is a constant. However, none of the above mentioned authors have explicitly studied the compatibility of the new expressions for τ which they use with the constancy in the values of $\tau T/\zeta$ at different temperatures. Recently, (Sinha *et al.*, 1964) from a study of the temperature dependence of τ-value of nitrobenzene and metanitrotoluene in dilute solutions in medicinal paraffin, it has been suggested that η^γ (where γ is the ratio of the molar activation energies for dielectric relaxation and viscous flow) may be a measure of the internal friction. In order to test the general validity of this suggestion and also to find out how the times of relaxation are related to the macroscopic viscosity, the present investigation on the measurement of dielectric loss in dilute solutions of some substituted nitrobenzenes in different non-polar solvents having high as well as low macroscopic viscosity at different temperatures was undertaken in the frequency region of 38.8KMc/s. The results obtained are discussed in this paper.

EXPERIMENTAL

All the substituted nitrobenzenes (*o*-, *m*- and *p*-nitrotoluene, *o*-, *m*- and *p*-chloronitrobenzenes, 2,5-dichloronitrobenzene and 1-Cl-2,4-dinitrobenzene) studied in the present investigation were of chemically pure quality. The liquid compounds were fractionally distilled and the proper fractions were dried by usual method while the solid compounds were purified by repeated crystallisations. The solvents used were CCl_4, C_6H_6, *n*-hexane and medicinal paraffin. The dried solvents showed negligible loss in the frequency region investigated. The experimental arrangements and the method of calculation of loss tangent (tan δ) were the same as described in an earlier paper (Bhattacharyya *et al.*, 1964).

RESULTS AND DISCUSSION

The values of times of relaxation (τ) for the various compounds in solutions in different solvents and at different temperatures (T) have been calculated from the experimental tan δ values with the help of the Debye equation for dilute solutions,

$$\tan \delta = \frac{(\epsilon'+2)^2}{\epsilon'} \cdot \frac{4\pi N c \mu^2}{}$$

where the various symbols have their usual significance. The values of the dipole moments (μ) of the different polar compounds and the dielectric constant (ϵ') of the solvents have been taken from the standard literature. The calculated values of τ together with the values of temperature (T) and loss tangent (tan δ) are given in Tables I - -IX.

The values of molar heats of activation ΔH_τ and ΔH_η for dielectric relaxation and viscous flow respectively (Eyring *et al.*, 1941) have been determined from the plots of log ($T\tau$) and log η against $1/T$ as usual. Some of the graphs are shown in Fig., 1a, 1b and 1c.

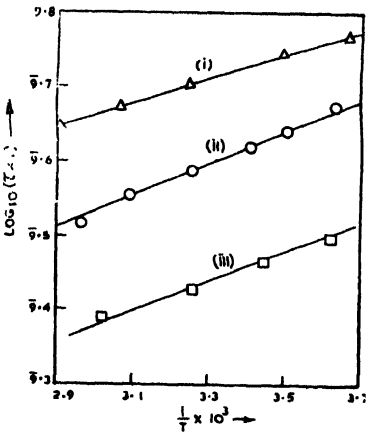

Fig. 1a. Plots of $\log_{10}$ (τT) vs $1/T$
Curve (*i*) Solution of orthochloronitrobenzene in CCl_4.
Curve (*ii*) Solution of orthochloronitrobenzene in C_6H_6.
Curve (*iii*) Solution of orthochloronitrobenzene in C_6H_{14}.

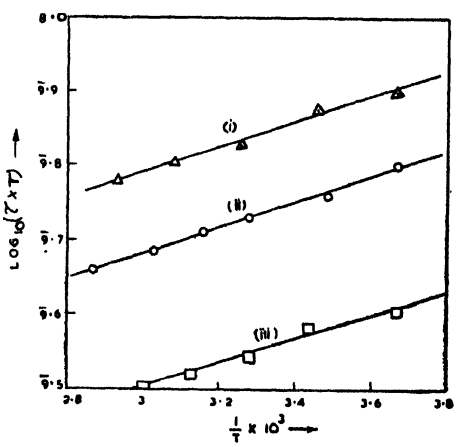

Fig. 1b. Plots of $\log_{10}$ (τT) vs $1/T$.
Curve (*i*) Solution of metanitrotoluene in CCl_4
Curve (*ii*) Solution of metanitrotoluene in C_6H_6
Curve (*iii*) Solution of metanitrotoluene in C_6H_{14}

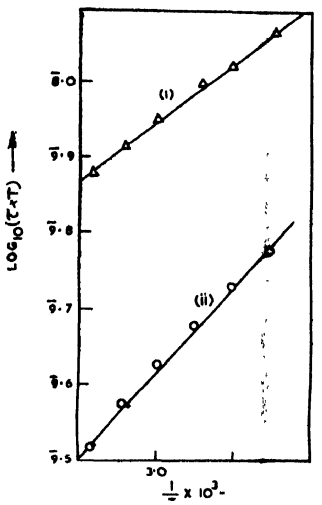

Fig. 1c. Plots of $\log_{10}(\tau T)$ vs $1/T$
Curve (*i*) Solution of metanitrotoluene in medicinal paraffin
Curve (*ii*) Solution of orthochloronitrobenzene in medicinal paraffin.

The value of ΔH_τ for a particular compound in a given solvent together with the value of ΔH_η for the solvent are given at the foot of the table for the particular compound.

It can be seen from the Tables that the τ-values for a given compound at any temperature in different solvents, increase in the order $\tau CCl_4 > \tau C_6H_6 > \tau C_6H_{12}$ for all the nitrobenzenes. From the Debye relation $\tau = \frac{\zeta}{2KT}$, it is evident that $\zeta CCl_4 > \zeta C_6H_6 > \zeta C_6H_{12}$. Since the macroscopic viscosities of the solvents increase in the same order viz $\eta CCl_4 > \eta C_6H_6 > \eta C_6H_{12}$, it may reasonably be concluded that ζ is functionally dependent on η. However, this dependence is not a linear one because the values of $\frac{\tau T}{\eta}$ for the different compounds in solutions in the various solvents do not remain constant but increase with increase of temperature or decrease in the value of viscosity. We may, therefore, put $\zeta = \phi(\eta)$. Substituting this value in the relation $\tau = \frac{\zeta}{2KT}$, we get $\frac{\tau T}{\phi(\eta)} = \frac{1}{2K} = \text{const.}$ and therefore, $\frac{d}{dT}\left[\frac{\tau T}{\phi(\eta)}\right] = 0$. This equation in conjunction with the relations due to Eyring *et al* (1941).

$$\tau = \frac{A}{T} \cdot e^{\Delta H_\tau / RT} \tag{1}$$

$$\eta = B \cdot e^{\Delta H_\eta / RT} \tag{2}$$

TABLE I

o-Chloronitrobenzene

Sol. in CCl_4 (1.7×10^{-4} mole/cc)				Sol. in C_6H_6 (1.7×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.7×10^{-4} mole/cc)			
T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec.	$\frac{\tau.T}{\eta^\gamma}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau.T}{\eta^\gamma}\times10^7$
273	33.5	21.46	26.80	275	40.9	17.2	20.81	276	57.1	11.4	16.49
286	34.9	19.48	27.23	285	43.5	15.3	20.38	290	59.4	10.1	16.46
308	37.9	16.38	27.10	293	45.0	14.2	20.48	307	61.7	8.8	16.54
326	39.8	14.50	27.08	307	47.5	12.6	20.43	331	63.0	7.5	16.79
344	41.6	12.88	27.10	323	50.2	11.0	20.45	—	—	—	—
ΔH_τ = 0.73K Cal/mole				ΔH_τ = 0.97K Cal/mole.				ΔH_τ = 0.90K Cal/mole.			
ΔH_η = 2.44K Cal/mole.				ΔH_η = 2.53K Cal/mole.				ΔH_η = 1.84K Cal/mole.			

TABLE II

m-Chloronitrobenzene

Sol. in CCl_4 (1.27×10^{-4} mole/cc)				Sol in C_6H_6 (1.27×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.27×10^{-4} mole/cc)			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta^2} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta^2} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta^2} \times 10^7$
274	15.2	20.74	20.13	273	19.0	16.20	19.19	273	28.4	9.80	11.62
288	15.8	18.73	21.10	284	19.7	14.89	19.66	286	29.7	8.59	11.48
298	16.3	17.50	21.64	294	20.6	13.60	19.75	294	30.1	7.99	11.61
308	17.4	15.63	21.00	307	21.7	12.43	20.10	308	30.6	7.13	11.82
320	18.3	14.10	20.95	320	22.6	10.90	19.55	319	31.1	6.38	11.70
331	18.7	13.16	21.22	336	23.5	9.75	20.04	338	31.5	5.14	11.08
345	19.2	12.15	21.85	352	24.6	8.35	19.12	—	—	—	—
$\Delta H_\tau = 0.97$K Cal/mole.				$\Delta H_\tau = 0.96$K Cal mole.				$\Delta H_\tau = 1.13$K Cal/mole.			
$\Delta H_\eta = 2.44$K Cal/mole.				$\Delta H_\eta = 2.53$K Cal/mole.				$\Delta H_\eta = 1.84$K Cal/mole.			

TABLE III

p-Chloronitrobenzene

Sol. in CCl_4 (2.13×10^{-4} mole/cc)				Sol. in C_6H_6 (1.94×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.27×10^{-4} mole/cc)			
T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau\cdot T}{\eta^2}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau\cdot T}{\eta^2}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau\cdot T}{\eta^2}\times10^7$
275	11.5	28.6	35.38	273	11.8	25.5	33.75	274	14.9	12.0	14.42
286	11.9	26.6	36.29	287	12.1	23.4	35.22	285	15.7	10.7	14.20
296	12.3	24.8	36.80	295	13.1	21.0	33.90	295	16.5	9.5	13.96
307	13.0	22.3	35.86	307	13.3	19.8	34.90	309	16.9	8.6	14.35
317	13.4	21.0	36.39	320	13.7	18.4	35.78	319	17.3	7.8	14.30
333	13.7	19.8	38.15	333	14.0	17.4	37.03	334	17.7	6.8	14.15
347	14.5	17.4	36.75	348	14.4	14.8	34.91	—	—	—	—
ΔH_τ = 0.76K Cal/mole.				ΔH_τ = 0.83K Cal/mole.				ΔH_τ = 1.12K Cal/mole.			
ΔH_η = 2.4K Cal/mole.				ΔH_η = 2.53K Cal/ mole.				ΔH_η = 1.85K Cal/mole.			

TABLE IV

o-Nitrotoluene

Sol. in CCl_4 (1.69×10^{-4} mole/cc)				Sol. in C_6H_6 (1.69×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.69×10^{-4} mole/cc)			
T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau\cdot T}{\eta^2}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec	$\frac{\tau\cdot T}{\eta_\gamma}\times10^7$	T°K	$\tan\delta\times10^3$	$\tau\times10^{12}$ Sec.	$\frac{\tau\cdot T}{\eta^2}\times10^7$
275	26.8	21.5	11.33	280	36.5	13.1	12.14	279	53.3	9.8	10.65
284	27.9	19.9	11.91	286	38.2	12.3	12.30	289	54.6	8.8	10.64
298	32.3	16.0	11.65	295	39.9	10.9	12.22	297	55.9	8.3	10.99
308	35.3	13.9	11.37	308	41.5	9.7	12.29	308	58.4	7.2	10.60
319	36.6	12.7	11.81	323	44.3	8.2	12.24	325	60.9	5.7	10.01
328	38.6	11.5	11.66	328	49.8	7.9	12.13	—	—	—	—
341	40.2	10.4	12.12	—	—	—	—	—	—	—	—

$\Delta H_\tau = 1.55$K Cal/mole.
$\Delta H_\eta = 2.44$K Cal/mole.

$\Delta H_\tau = 1.35$K Cal/mole.
$\Delta H_\eta = 2.53$K Cal/mole.

$\Delta H_\tau = 1.33$K Cal/mole.
$\Delta H_\eta = 1.84$K Cal/mole.

TABLE V

m-Nitrotoluene

Sol. in CCl_4 (1.7×10^{-4} mole/cc)				Sol. in C_6H_6 (1.7×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.7×10^{-4} mole/cc)			
T°m	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau . T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec.	$\frac{\tau . T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau . T}{\eta^\gamma} \times 10^7$
273	25.0	29.17	34.58	273	30.4	23.02	31.80	273	46.9	14.77	22.76
289	26.2	26.06	35.72	287	32.6	20.15	31.50	291	48.0	13.20	23.30
307	29.0	21.95	34.51	305	34.8	17.60	31.64	305	51.7	11.45	22.53
324	30.4	19.68	35.02	318	35.9	16.21	32.01	320	53.31	10.33	22.74
341	31.8	17.73	35.46	330	37.6	14.72	31.49	333	54.10	9.56	22.86
—	—	—	—	—	—	—	—	—	—	—	—

$\Delta H_\tau = 0.78K$ Cal/mole. $\Delta H_\eta = 2.44K$ Cal/mole.

$\Delta H_\tau = 0.79K$ Cal/mole. $\Delta H_\eta = 2.53K$ Cal/mole.

$\Delta H_\tau = 0.78K$ Cal/mole. $\Delta H_\eta = 1.84K$ Cal/mole.

TABLE VI

p-Nitrotoluene

Sol. in CCl_4 (1.46×10^{-4} mole/cc)				Sol. in C_6H_6 (1.46×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.46×10^{-4} mole/cc)			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec.	$\frac{\tau . T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau . T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau . T}{\eta^\gamma} \times 10^7$
275	18.9	36.55	40.74	273	22.9	29.7	38.48	273	38.9	19.1	28.24
288	20.8	31.71	40.17	288	25.1	25.3	37.51	288	40.6	17.2	28.64
307	23.0	26.69	39.41	307	27.3	21.8	37.72	307	44.2	14.6	28.21
328	24.5	23.30	40.24	320	28.0	20.2	38.77	329	46.5	12.6	28.51
343	26.0	20.83	40.13	334	30.2	17.8	36.61	—	—	—	—
—	—	—	—	350	32.4	15.6	36.71	—	—	—	—
$\Delta H_\tau = 0.85$K Cal/mole. $\Delta H_\eta = 2.44$K Cal/mole.				$\Delta H_\tau = 0.86$K Cal/mole. $\Delta H_\eta = 2.53$K Cal/mole.				$\Delta H_\tau = 0.82$K Cal/mole. $\Delta H_\eta = 1.84$K Cal/mole.			

TABLE VII

2, 5-dichloronitrobenzene

Sol. in CCl_4 (1.331×10^{-4} mole/cc)				Sol. in C_6H_6 (1.321×10^{-4} mole/cc)				Sol. in C_6H_{14} (1.081×10^{-4} mole cc)			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec.	$\frac{\tau \cdot T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec.	$\frac{\tau \cdot T}{\eta^\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta^\gamma} \times 10^7$
277	10.8	35.8	17.58	275	14.2	26.9	27.38	278	19.8	14.3	12.92
288	11.6	31.3	18.21	286	15.2	23.5	26.95	288	21.3	12.6	12.80
297	13.2	26.5	17.46	297	16.2	21.1	27.19	296	22.6	11.3	12.65
307	14.5	23.0	17.04	307	17.6	18.5	26.21	308	23.7	10.6	13.24
320	15.5	20.5	17.81	319	18.4	17.0	26.81	319	24.7	8.9	13.20
327	16.3	18.9	17.74	331	19.0	15.7	27.45	333	26.9	7.2	12.31
337	16.9	17.6	18.40	347	20.2	13.8	27.71	—	—	—	—

$\Delta H_\tau = 1.67$K Cal/mole. $\Delta H_\eta = 2.44$K Cal mole.

$\Delta H_\gamma = 1.17$K Cal/mole. $\Delta H_\eta = 2.53$K Cal/mole.

$\Delta H_\tau = 1.57$K Cal/mole. $\Delta H_\eta = 1.84$K Cal molei

TABLE VIII

1-Chloro, 2, 4-dinitrobenzene

Sol. in CCl_4 (9.97×10^{-5} mole/cc)				Sol. in C_6H_6 (1.25×10^{-4} mole/cc)			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec.	$\frac{\tau \cdot T}{\eta\gamma} \times 10^7$
277	7.0	33.4	17.70	276	9.6	30.7	17.78
288	7.9	28.6	17.88	285	10.6	26.8	17.74
295	8.5	25.9	17.78	292	11.5	24.0	17.77
304	9.3	22.6	17.37	297	12.1	22.2	17.74
313	9.7	20.9	17.74	305	13.4	19.6	17.32
321	10.1	19.4	18.05	315	14.3	17.7	17.68
332	11.1	16.9	17.56	323	15.3	15.7	17.45
345	11.7	15.1	18.13	335	16.2	14.1	17.78
ΔH_τ = 1.58K Cal/mole.				ΔH_τ = 1.85K Cal/mole.			
ΔH_η = 2.44K Cal/mole.				ΔH_η = 2.53K Cal/mole.			

TABLE IX

3% Solution in Paraffin

Metanitrotoluene				Orthochloronitrobenzene			
T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta\gamma} \times 10^7$	T°K	$\tan\delta \times 10^3$	$\tau \times 10^{12}$ Sec	$\frac{\tau \cdot T}{\eta\gamma} \times 10^7$
303.	25.8	38.4	27.09	304.	38.5	19.8	7.46
313	28.4	33.6	27.72	313	42.4	17.2	7.81
321	30.3	30.7	28.08	323	46.9	14.8	8.04
333	33.3	26.8	28.26	333	51.9	12.7	8.00
343	35.9	24.0	28.32	343	56.4	11.0	8.07
353	38.5	21.6	28.04	353	61.4	9.4	7.79
ΔH_τ = 1.83K Cal/mole.				ΔH_τ = 2.66K Cal/mole.			
ΔH_η = 6.33K Cal/mole.				ΔH_η = 6.33K Cal/mole.			

yields

$$\frac{d\phi}{\phi} = \gamma \cdot \frac{d\eta}{\eta}$$

where $\frac{\Delta H\tau}{\Delta H_n}$.

In equation (2) the factor B is assumed to be independent of temperature within the range under investigation.

Integration of this equation gives $\phi(\eta) = D\eta^{\gamma}$ where D is a constant. Thus $\zeta = D\eta^{\gamma} = \frac{D}{\eta^{1-\gamma}} \cdot \eta$ and since ζ has the dimension of erg. sec. and η that of poise ($ML^{-1}T^{-1}$) it is seen that $D/\eta^{1-\gamma}$ must have the dimension of a volume (L^3).

It is evident that D contains a factor which has the same dimension as that of $\eta^{1-\gamma}$ and another factor having the dimension of volume. So D may be written as $D = C\eta_0^{1-\gamma}$ where C and η_0 are constants for a a particular compound in a particular solvent. C has the dimension of volume and η_0 is in poise so that $\left(\frac{\eta_0}{\eta}\right)^{1-\gamma}$ is a pure fraction.

Thus $\zeta = D\eta^{\gamma} = C\left(\frac{\eta_0}{\eta}\right)^{1-\gamma} \eta = 2\tau KT$. and

$$\frac{\tau T}{\eta^{\gamma}} = \frac{C}{2K} \eta_0^{1-\gamma} \tag{3}$$

The above equation shows that $\frac{\tau T}{\eta^{\gamma}}$ should be a constant for a given polar solute in solution in a given non-polar solvent for all temperatures. Actually, it is found from the Tables that the values of $\frac{\tau T}{\eta^{\gamma}}$ are constants which are different in different cases. The values of C and η_0 can not be determined at present but if $\gamma = 1$, it is seen that $\tau = \frac{C \cdot \eta}{2KT}$ which has the same form as the usual expression for τ viz $\tau = \frac{3V}{KT} \cdot \eta$. For other values of γ if $\left(\frac{\eta_0}{\eta}\right)^{1-\gamma} \cdot \eta$ is put equal to $\eta_{int.}$, τ can be written in the form $\tau = \frac{C}{2KT} \cdot \eta_{int.}$ This expression for η_{int} at once shows why the value of the constant in Fischer's assumption $\eta_{int.} = \text{const.}$ η has to be different for different solvents. From these consideration it may be concluded that η^{γ} may be taken to be a measure of internal frictions as has been suggested earlier (Sinha *et al*, 1964). But it should be noted that the value of γ in the latter case is different from that in the present case.

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